

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of : Shinji Matsuo ; Hiroshi Miyazaki

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Group Art Unit : 1794

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner for patents

Alexandria, Virginia 22313-1450

Sir:

Now comes Hiroshi Miyazaki who declares and says that:

1. I am a co-inventor of the United States Patent Application Serial Number 11/660,673.
2. I graduated from Hokkaido University, Faculty of Science, department of Chemistry in 1986.
3. I have been employed by Nippon Steel Chemical Co., Ltd. since 1986, and I investigated the syntheses and development of novel organic compounds and the development of the organic electroluminescent device.

1) Preface

Organic EL occurs via fluorescence or phosphorescence. In the case of fluorescence, a fluorescent material is used alone or doped on a host material for the light-emitting layer. In the case of phosphorescence, a phosphorescent material is frequently used after doping on a host material as phosphorescent materials are generally unstable.

In consequence, in selecting a material constituting the light-emitting layer, a combination of a host material and a guest material is important in either fluorescence or phosphorescence; however, a material that has been known to be effective for constituting the light-emitting layer in a fluorescent device is not necessarily effective as a host material in phosphorescence and this topic will be discussed below.

2) Opinion Offered by a Specialist

In the case where a guest material and a host material are used in the light-emitting layer of an organic electroluminescent device, the host material is first excited from the ground state S_0 to the singlet excited state S_1 and the triplet excited state T_1 (the probability of existence in respective state is theoretically 1:3) upon recombination of the electrons and the holes injected from the electrodes, energy is then transferred from the host material to the guest material, and the guest material is excited to emit light.

There are two kinds of mechanisms for this energy transfer and, as illustrated in Fig. 1, energy is transferred to the guest material (dopant) by the intermolecular energy transfer mechanisms called the "Forster mechanism (= dipole - dipole interaction)" and the "Dexter mechanism (= electron exchange

interaction).”

According to the Forster mechanism, the energy transfer occurs between the host material in the excited state and the guest material in the ground state by resonance of the dipole vibration, comparable to resonance of a tuning fork; the energy transfer from S_1 of the host material to S_1 of the guest material is allowed, but the energy transfer from T_1 of the host material to T_1 of the guest material is prohibited. Moreover, the efficiency of energy transfer is influenced by overlapping of the emission spectrum of the host material and the absorption spectrum of the guest material. Further, the distance of transfer is said to reach 10 nm at the longest and the transferred energy is irreversible.

According to the Dexter mechanism, the energy transfer occurs by exchange of wave motion in the molecules coming nearer to one another and the energy transfer from S_1 of the host material to S_1 of the guest material and the energy transfer from T_1 of the host material to T_1 of the guest material are allowed. The overlapping of molecular orbitals and the energy level of the orbitals are important for efficient energy transfer.

Furthermore, in the case of fluorescence, light is emitted when the guest material returns from S_1 to S_0 , but light is not emitted when the guest material returns from T_1 to S_0 because energy is consumed by thermal deactivation or the like. Therefore, the energy transfer to S_1 of the guest material assumes importance; it is important that S_1 of the host material is higher than S_1 of the guest material and T_1 of the host material is not important. Further, if energy transfer occurs by the Forester mechanism as illustrated in Fig. 1, energy transfer is permitted to occur only from S_1 of the host material to S_1 of the guest material and light is emitted when the guest material returns from S_1 to

S_0 . Even if energy transfer occurs by the Dexter mechanism, only S_1 of the guest material to which energy is transferred from the host material becomes involved in emission of light and T_1 does not contribute to emission of light.

On the other hand, in the case of phosphorescence, light is emitted when the guest material returns from T_1 to S_0 . Therefore, energy transfer to S_1 and T_1 of the guest material assumes importance; it is important that S_1 and T_1 of the host material are respectively higher than S_1 and T_1 of the guest material and, in particular, T_1 of the host material becomes important. As illustrated in Fig. 1, energy transfer of T_1 can occur only by the Dexter mechanism and the Dexter mechanism becomes important in the case of phosphorescence wherein the transferred energy consists of the one transferred from T_1 of the host material to T_1 of the guest material (75% of the total) and another one transferred from S_1 of the guest material to T_1 of the guest material (25% of the total) and the luminous efficiency in phosphorescence becomes approximately three times that in fluorescence.

That is, a fluorescent device (F-OLED) differs greatly from a phosphorescent device (P-OLED) in the mechanism of emission of light as light is emitted when $S_1 \Rightarrow S_0$ in fluorescence while light is emitted when $T_1 \Rightarrow S_0$ in phosphorescence. Further, a guest material (a light-emitting material or a dopant) which has a function of emitting light by itself differs entirely in function from a host material which has a function of transferring electrical charges or energy efficiently to a guest material. Therefore, there would be no motivation at all to apply either a fluorescent guest material which emits light by itself (a fluorescent material or a fluorescent dopant) or a material which is known to be a host material for fluorescence as a phosphorescent host material

and it would be difficult even for a person skilled in the art to forecast the efficiency of such an application for the reason that S_1 of the host material is important in fluorescence while T_1 is important in phosphorescence.

In order to help one understand the action of a highly efficient phosphorescent device, the energy transfer from the host material to the guest material of a P-OLED is schematically shown in Fig. 2.

As shown in Fig. 2, the energy transferred from a host material having a sufficiently high triplet excitation energy (T_1) is converted to light efficiently or this case constitutes an efficient host-guest system; however, the mechanism involved in the case of a poor host-guest system wherein T_1 of the guest material is lower than T_1 of the host material differs from the aforementioned Forster mechanism and the energy flows in the reverse direction in spite of overlapping of emission spectra thereby causing a marked drop in the efficiency.

Two examples in Fig. 2 show that an efficient host-guest system is not provided and phosphorescence cannot occur sufficiently unless T_1 of the host material is high. When T_1 of the host material is low, a poor host-guest system prevails and light is not emitted sufficiently. That is to say, many of the guest materials and host materials known for F-OLEDs have low T_1 and tend to provide a poor system and, when they are applied as host materials for P-OLEDs, they cannot be made to cause phosphorescence. An example in point is Alq3; it is typically a good guest material or a good host material for F-OLEDs, but it cannot be used as a host material for P-OLEDs. On the other hand, a combination of Alq3 as a host material for F-OLEDs and another

fluorescent material as a guest material provides a good host material as the mechanism of energy transfer differs in the case of F-OLEDs as described above. That is, a given guest material differs greatly in its characteristics as a light-emitting material depending on whether it is used in F-OLEDs or P-OLEDs.

Reference 1 (SID 04 DIGEST 901-903) is cited as a concrete example. As illustrated in Table 1 of Reference 1, Alq3 that has an excellent ability as a host material for F-OLEDs cannot perform sufficiently when used as a host material for P-OLEDs. This is because a poor host-guest system comes into existence wherein the excitation energy T_1 of the dopant flows in the reverse direction to the low triplet excitation energy (T_1) orbital of Alq3 according to the Dexter mechanism.

The aforementioned description refers to an instance wherein a high-performance host material for F-OLEDs does not function as a host material for P-OLEDs.

3) Conclusion

It is apparent from the aforementioned explanation that the applicability of a light-emitting material for F-OLEDs as a host material for P-OLEDs is not self-evident; for example, even when a certain light-emitting material is known as a host material for F-OLEDs, its applicability as a host material to P-OLEDs cannot be self-evident.

In order to transfer energy efficiently to the guest material to cause

emission of light, it is important to have an adequate combination of a host material and a guest material and it is important to select a host material best suited for either a fluorescent guest material or a phosphorescent guest material. Normally, a host material is selected from electrical charge-transporting materials whose number is enormous. In consequence, a large number of experiments are required in selecting materials specifically known as light-emitting materials for F-OLEDs from a vast number of electrical charge-transporting materials and this is a difficult task.

It is to be noted that the P-OLED of this invention corresponds to the efficient host-guest system shown in Fig. 2 and emits phosphorescence at high efficiency.

Fig. 1

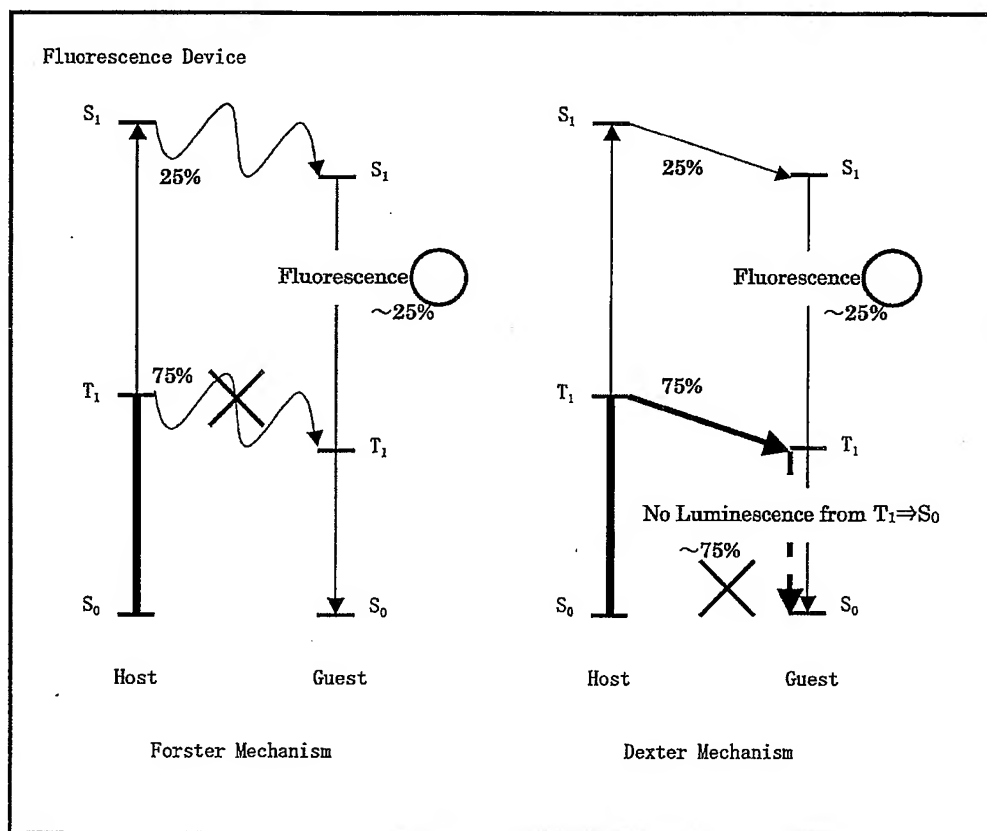
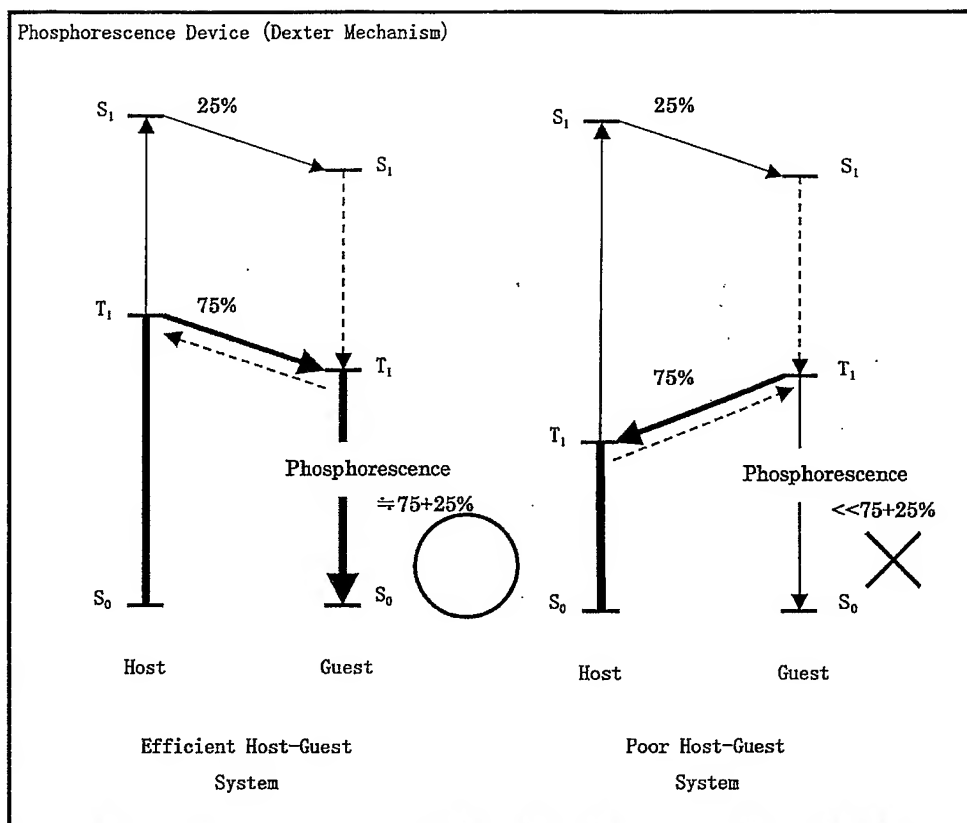


Fig. 2



Attachment : Reference 1 (SID 04 DIGEST 901-903)

I, the undersigned petitioner, further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This 18th day of January 2010

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23.3: Distinguished Paper: Red-Phosphorescent OLEDs Employing Bis(8-Quinolinolato)-Phenolato-Aluminum(III) Complexes as Emission-Layer Hosts

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Abstract

We have developed high-efficiency, long-lived organic light-emitting diode (OLED) devices by introducing red phosphorescent dopants into bis(8-quinolinolato)phenolato-aluminum(III) complexes. The devices exhibited luminance efficiency of 12 cd/A at CIE color coordinates (0.65, 0.34). The luminance half-decay lifetime is expected to be over 30,000 hours at an initial luminance of 700 cd/m². We have successfully incorporated these devices into commercial OLED displays.

1. Introduction

Various high-efficiency organic light-emitting diode (OLED) devices using phosphorescent emitting materials have been proposed [1-7]. Very high external quantum efficiency of 19% has been attained using bis(2-phenylpyridine)iridium acetylacetonate [5]. Suppose light out-coupling efficiency is 20%, the internal quantum efficiency comes close to 100%. We can thus realize high brightness, low power consumption displays by using phosphorescent OLED devices.

The emission layer of phosphorescent OLED devices is generally composed of a carbazole-type host doped with phosphorescent dopants. 4,4'-N,N'-dicarbazol-biphenyl (CBP) is a typical host material. The exciton formation zone of the devices extends over 30 nm because of the bipolar carrier transporting ability of CBP. A hole blocking layer is needed to confine holes and excitons in the emission layer for high efficiency.

The operating lifetime of phosphorescent OLED devices in an earlier report was about 170 hours [3]. The limit on the lifetime was attributed to instability of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), which was incorporated between an emission layer and an electron transport layer as a hole blocking layer. Replacing BCP with bis(2-methyl-8-quinolinolato)(p-phenylphenolato)aluminum (BALq) improves the operating lifetime of phosphorescent OLED devices [7].

The use of electron-transporting materials, such as BCP, as emission layer hosts has also been proposed [4-5]. The exciton formation zone is very narrow in BCP host devices. Excitons form only at the interface between a hole transport layer and an emission layer, and diffuse within a range of about 15 nm. Confinement of triplet excitons in the narrow area promotes triplet-triplet annihilation. Besides, as mentioned above, BCP is an unstable material and, for example, apt to crystallize. There is no hope of achieving a long operating lifetime. However, the structure of electron-transporting host devices is compatible with that of fluorescent devices, which have no hole blocking layer.

The device structure without a hole blocking layer is a fascinating and promising one for commercial production of OLED displays.

Here, we discuss the use of bis(8-quinolinolato)phenolato-aluminum complexes as emission layer hosts which have dominant electron-transporting ability.

2. OLED device fabrication

The device structure and typical materials in this study are shown in Figure 1. The OLEDs were fabricated by a conventional evaporation method at a chamber pressure of about 5×10^{-6} torr. Organic materials were evaporated onto an ITO-coated glass substrate. 4,4'-bis(N-(naphthyl)-N-phenyl-amino)biphenyl (NPB) was used as a hole transport layer. Copper phthalocyanine (CuPc) was inserted as a hole injection layer between ITO and NPB if necessary for device durability [8]. Bis(8-quinolinolato)phenolato-aluminum complexes, such as BALq, were used as an emission layer host and doped with a red phosphorescent dopant at a concentration of 7 wt%. Tris(8-quinolinolato)aluminum (Alq₃) was used as an electron transport layer. Li₂O was deposited onto the Alq₃ layer as an electron injection material. Finally, an aluminum cathode was deposited onto the alkaline metal compound layer. The layer thickness of these organic materials was optimized for luminous efficiency by adjusting the optical distances between emission sites and dominant reflective surfaces; i.e., the organic layer / cathode and ITO / glass interfaces [9]. The emitting area of the devices was 2 mm x 2 mm.

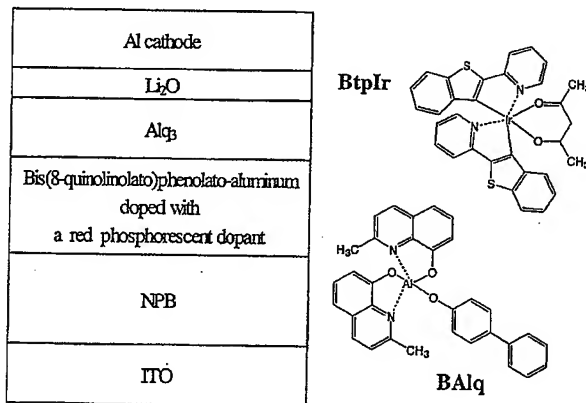


Figure 1. Device structure and typical materials in this study.

3. Results and discussion

3.1 Characterization of electron-transporting host materials

First, we used BAQ as a host material and doped it with bis(2-(2'-benzo[4,5- α]thienyl) pyridinato-N,C^{3'})iridium acetylacetonate (BtpIr), a red phosphorescent dopant [6]. The device structure was ITO (110 nm)/NPB (80 nm)/BtpIr-doped BAQ (47.5 nm)/Alq₃ (30 nm)/Li₂O (0.5 nm)/Al (100 nm). We also employed Alq₃, BCP, and 1,3-bis(N,N-*t*-butyl-phenyl)-1,3,4-oxadiazole (OXD-7) as host materials for comparison. Electroluminescent characteristics of the devices are summarized in Table 1. The BAQ device exhibited the highest external quantum efficiency (8.6%) in these electron-transporting hosts.

We ascribed the low efficiency of the Alq₃ host devices to the lower triplet energy level of Alq₃ compared to that of BtpIr. This was not the case, though, for the BCP host device or the OXD-7 host device. BCP and OXD-7 have sufficiently high triplet energy levels for the dopant [4]. The low efficiency was because of the narrow exciton-formation zone in these devices. The narrow exciton-formation zone promoted triplet-triplet annihilation and energy migration from an emission-layer to the adjacent NPB layer.

We varied the emission-layer (EML) thickness of BAQ host devices from 10 nm to 70 nm while maintaining the total thickness of the EML and Alq₃ layers at 77.5 nm. Figure 2 shows the external quantum efficiency and CIE_x color coordinates of the devices as a function of EML thickness, compared with those of BCP host devices. In the BAQ host devices, external quantum efficiency and CIE_x increased with EML thickness and were saturated only after the EML thickness was 40 nm or more. On the other hand, the external quantum efficiency and CIE_x for BCP host devices saturated at an EML thickness of 15 nm. These results show that the BAQ host devices had a wide emission zone.

We next investigated the operating lifetime of the BAQ host device. The luminance decay curve of the device under continuous constant current driving of 2.5 mA/cm² is shown in Figure 3. The half-decay lifetime of the device was 13,000 hours at an initial luminance of 180 cd/m². Figure 3 also shows the luminance decay curve of a CBP host device having a structure of ITO (110 nm)/NPB (60 nm)/BtpIr-doped CBP (30 nm)/BAQ (10

Table 1. Electroluminescent characteristics of the devices having electron-transporting hosts.

Hosts	Driving current density of 2.5 mA/cm ²				Voltage V
	Color coordinates CIE _x CIE _y	Luminance cd/m ²	E.Q.E. %		
Alq ₃	0.684 0.316	42	2.2		4.4
BAQ	0.680 0.319	179	8.6		6.5
BCP	0.680 0.319	133	6.1		5.3
OXD-7	0.679 0.320	59	2.8		4.1

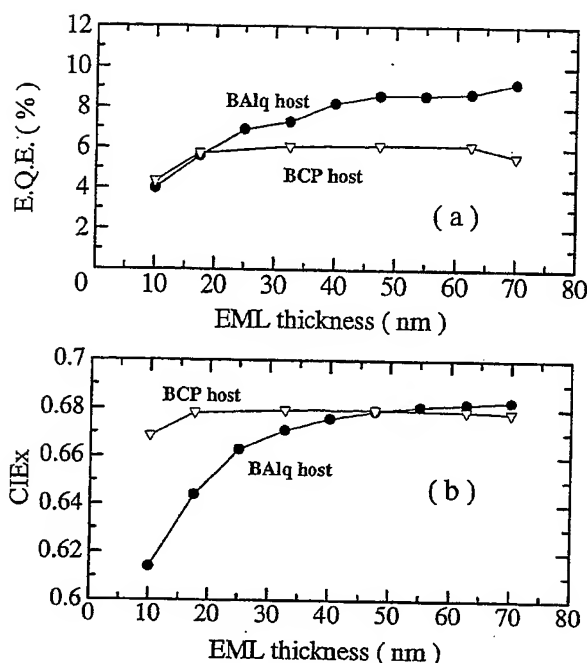


Figure 2. (a) External quantum efficiency and (b) CIE_x of BAQ host devices (closed circles) and BCP host devices (opened reverse-triangles) as a function of EML thickness.

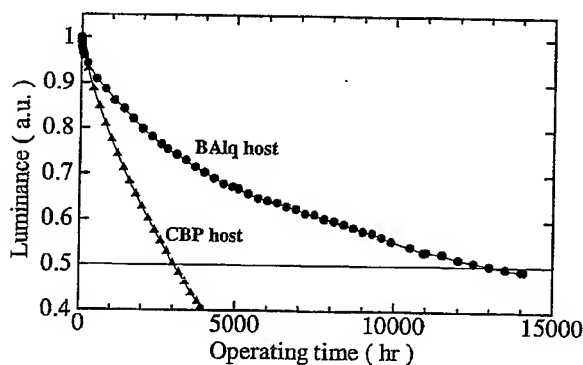


Figure 3. Luminance decay curves of the BAQ host device (closed circles) and the CBP host device (closed triangles). The devices were operated under continuous constant current driving of 2.5 mA/cm².

nm)/Alq₃ (65 nm)/Li₂O (0.5 nm)/Al (100 nm). The operating lifetime of the BAQ host device was four times that of the CBP host device.

Employing BAQ as an emission layer host resulted in high efficiency, long-lived red phosphorescent devices.

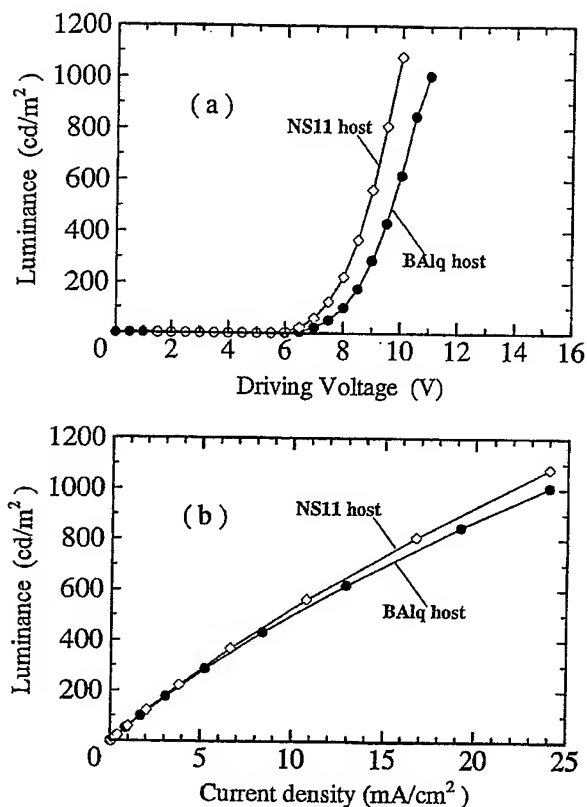


Figure 4. (a) Luminance-voltage characteristics and (b) luminance-current characteristics of the NS11 host device (opened diamonds) and the BALq host devices (closed circles). The device structure was ITO (110 nm)/CuPc (25 nm)/NPB (55 nm)/Host material doped with BtpIr (47.5 nm)/Alq₃ (65 nm)/Li₂O (0.5 nm)/Al (100 nm).

3.2 Modification of molecular structure in the complexes

The glass transition temperature of BALq is 99°C. Higher glass transition temperature is needed to ensure the stability of OLED displays in high temperature environments. We considered the synthesis of 50 kinds of bis(8-quinolinolato)-phenolato-aluminum complexes. Modification of the ligands – that is, two 8-quinolinolato ligands and a phenolato ligand – changed the glass transition temperature. Inappropriate introduction of substituents reduced the glass transition temperature contrary to our intention. Some bis(8-quinolinolato)phenolato-aluminum complexes, which have a glass transition temperature of 110°C or more, were successfully synthesized. One of these complexes exhibited good electroluminescent characteristics. This novel bis(8-quinolinolato)phenolato-aluminum complex was named NS11. The luminance-voltage characteristics and the luminance-current characteristics of NS11 host devices are shown in Figure 4. NS11 enhanced the luminance efficiency in the high current region and lowered the driving voltage in contrast to BALq.

3.3 Combination with UDC red phosphorescent dopant

We fabricated devices in which the emission layer was composed of NS11 doped with a novel red phosphorescent dopant provided by Universal Display Corporation. The device structure was ITO (110 nm)/CuPc (25 nm)/NPB (55 nm)/NS11 doped with the UDC red phosphorescent dopant (47.5 nm)/Alq₃ (30 nm)/Li₂O (0.5 nm)/Al (100 nm). The devices exhibited external quantum efficiency of 12% and luminance efficiency of 12 cd/A at the CIE color coordinates (0.65, 0.34). The luminance decay curve of the devices under continuous constant current driving of 5.5 mA/cm² is shown in Figure 5. The half-decay lifetime of the devices is expected to be over 30,000 hours at an initial luminance of 700 cd/m².

We also investigated the electroluminescent characteristics of the devices under 1/128 duty-ratio pulse driving, which is appropriate for passive matrix applications. The luminance-current characteristics are shown in Figure 6. The NS11 device doped with the UDC red phosphorescent dopant exhibited higher luminance efficiency than the red fluorescent device even at 300 cd/m², which is equivalent to a peak luminance of 38400 cd/m². There was no degradation of color purity in the NS11 device, maintaining the CIE color coordinates of (0.65, 0.34) in all the measured ranges. Clearly, the NS11 devices doped with the UDC red phosphorescent dopant are usable for passive matrix displays. On the other hand, the BALq device doped with BtpIr showed lower efficiency than the fluorescent devices under the pulse driving. We measured a photoluminescence transient lifetime of the UDC red phosphorescent dopant and BtpIr, which were doped into an NS11 matrix. The UDC red phosphorescent dopant showed a very short phosphorescent lifetime of 1.6 μ s, a quarter of the BtpIr lifetime. Both the wide emission zone enabled by NS11 and the short phosphorescent lifetime of the UDC red phosphorescent dopant reduced triplet-triplet annihilation.

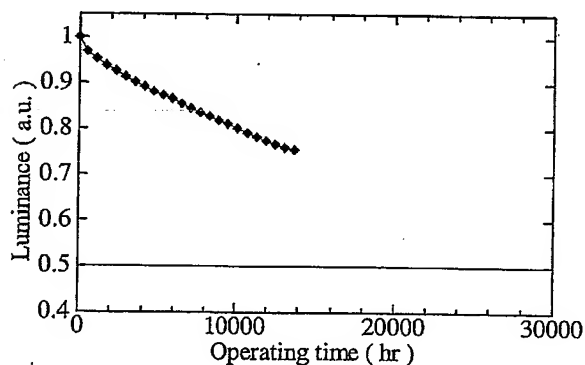


Figure 5. Luminance decay curve of an NS11 device doped with a UDC red phosphorescent dopant. The device was operated under continuous constant current driving of 5.5 mA/cm².

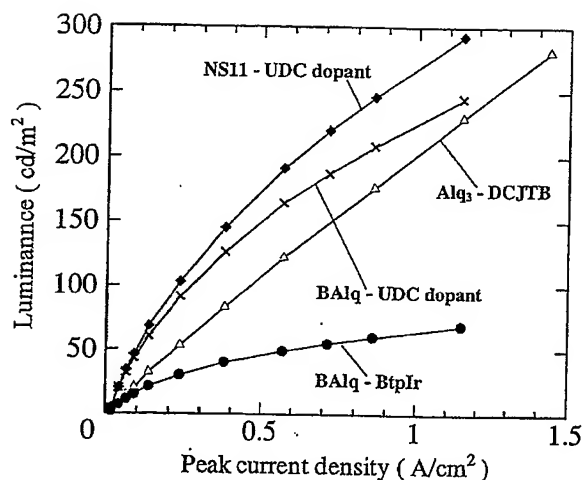


Figure 6. Luminance-current characteristics under 1/128 duty-ratio pulse driving. Devices shown in this figure are an NS11 device doped with a UDC red phosphorescent dopant (closed diamonds), a BALq device doped with a UDC red phosphorescent dopant (crosses), a BALq device doped with BtpIr (closed circles), and a red fluorescent device (opened triangles). The red fluorescent device had a structure of ITO (110 nm)/CuPc (25 nm)/NPB (55 nm)/DCJTb-doped Alq₃(40 nm)/Alq₃ (40 nm)/Li₂O (0.5 nm)/Al (100 nm).

3.4 Incorporation into commercial OLED displays

We incorporated NS11 devices doped with the UDC red phosphorescent dopant into commercial OLED displays. The OLED displays were then applied to the sub-display of cellular phones. The phosphorescent devices made the expression of reds more brilliant and improved the color reproducibility of the OLED displays.

The specifications of the commercial OLED display are:

Type	Passive matrix
Size	1.1 inch diagonal
Resolution	96 x RGB x 72
Colors	4096

4 Summary

We have used bis(8-quinolinolato)phenolato-aluminum complexes as emission-layer hosts in red phosphorescent OLED devices. This enabled high-efficiency, long-lived OLED devices with a simple device structure needing no hole-blocking layer. Devices with a UDC red phosphorescent dopant introduced into the NS11 exhibited high efficiency of 12 cd/A at CIE color coordinates (0.65, 0.34) and a long operating lifetime of 30,000 hours or more at an initial luminance of 700 cd/m². Moreover, triplet-triplet annihilation was reduced in the devices because of the wide emission zone enabled by NS11 and the short phosphorescent lifetime of a UDC red phosphorescent dopant. We have successfully incorporated these red phosphorescent devices into commercial OLED displays.

5 Acknowledgement

We wish to express our gratitude to Universal Display Corporation for providing us with high-performance phosphorescent materials.

6 References

- [1] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoutstikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature* **395**, 151 (1998)
- [2] M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.* **75**, 4 (1999)
- [3] T. Tsutsui, M. J. Yang, M. Yabito, K. Nakamura, T. Watanabe, T. Tsuji, Y. Fukuda, T. Wakimoto, S. Miyaguchi, *Jpn. J. Appl. Phys., Part 2* **38**, L1502 (1999)
- [4] C. Adachi, M. A. Baldo, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.* **77**, 904 (2000)
- [5] C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.* **90**, 5048(2001)
- [6] C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson and R. C. Kwong, *Appl. Phys. Lett.* **78**, 1622 (2001)
- [7] T. Watanabe, K. Nakamura, S. Kawami, Y. Fukuda, T. Tsuji, T. Wakimoto and S. Miyaguchi, *Proceedings of SPIE* **4105**, 175 (2000)
- [8] S. A. Van Slyke, C. H. Chen and C. W. Tang, *Appl. Phys. Lett.* **69**, 2160(1996)
- [9] Y. Fukuda, S. Miyaguchi, S. Ishizuka, T. Wakimoto, J. Funaki, H. Kubota, T. Watanabe, H. Ochi, T. Sakamoto, M. Tsuchida, I. Ohshita, H. Nakada and T. Tohma, *SID'99 Digest* 430 (1999)